# The Reduction by Deuterium on Platinum Black of exo-2-Norbornyl• and endo-2-Norbornyl• to Norbornane-2-d₁ Occurs with Predominant Retention of Configuration[1]

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The heterogeneous, platinum-catalyzed hydrogenation of (di-olefin)dialkylplatinum(II) complexes ((DO)PtR₂) on platinum black produces alkanes by reduction of the diolefin and alkyl-platinum moieties; the platinum(II) is reduced to platinum(0) and becomes part of the catalyst (eq 1).[2-5] This reaction involves (i)
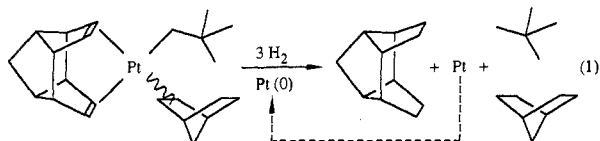


adsorption of $H_2$ and (DO)PtR₂ on the surface of the catalyst, (ii) generation of platinum surface alkyls from the alkyl and diolefin moieties of the (DO)PtR₂ complex, and (iii) reaction of the surface alkyls with surface hydrides to produce alkanes.

Although the stereochemical outcome of heterogeneous hydrogenations of olefins on noble metal catalysts is well studied,[6] the stereochemistry of reduction of the C• bond has remained a matter of inference. Addition of $H_2$ occurs cis, on the less hindered face of the olefin.[7-14] Since it is assumed that olefins coordinate by presenting their less hindered face to the surface of the metal, and that H• adds to this coordinated face, the inference from these results is that the reduction of the C• bond occurs with retention of configuration. Inferring the stereochemistry of reduction of the C• bond from the overall stereochemical course of the reduction of an olefin is, however, an uncertain process. We wished to determine directly the stereochemistry of the reaction C• + D• → CD.

This paper reports an investigation of the stereochemistry of the reduction of C• bonds in heterogeneous hydrogenations, based on the adsorption of (DO)PtR₂ on platinum black to generate R• groups. We synthesized samples containing predominantly (ho-
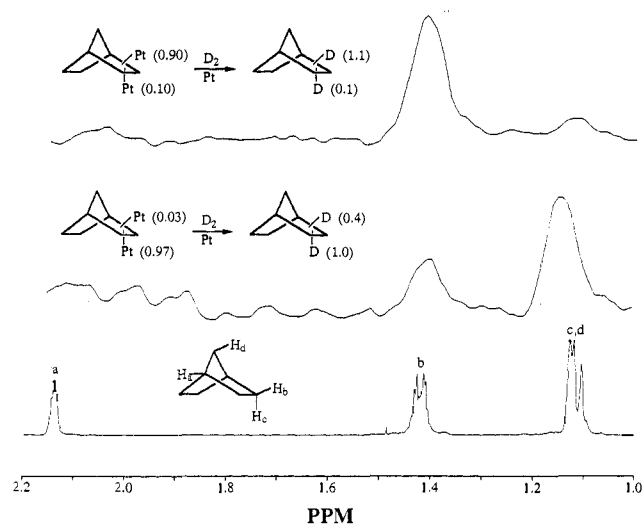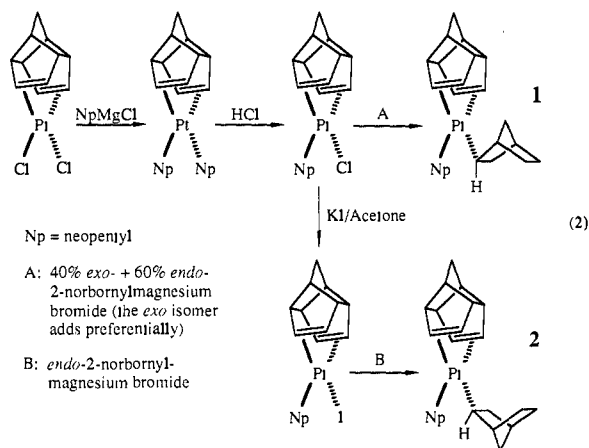
(1) The National Science Foundation (Grant CHE-88-12709), the Office of Naval Research, and the Defense Advanced Research Projects Agency supported this work.
(2) Miller, T. M.; Izumi, A. N.; Shih, Y.-S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3146–3156.
(3) Miller, T. M.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3156–3163.
(4) Miller, T. M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3164–3170.
(5) McCarthy, T. J.; Shih, Y.-S.; Whitesides, G. M. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 4649–4651.
(6) For reviews, see: Rylander, P. N. *Hydrogenation Methods*; Academic Press, Inc.: San Diego, 1985. Ozaki, A. *Isotopic Studies of Heterogeneous Catalysis*; Academic Press, Inc.: New York, 1977. Burwell, R. L., Jr. *Catal. Rev.* **1972**, *7*, 25–49. Rylander, P. N. *Catalytic Hydrogenation over Platinum Metals*; Academic Press, Inc.: New York, 1967.
(7) Eigenmann, G. W.; Arnold, R. T. *J. Am. Chem. Soc.* **1959**, *81*, 3440–3442.
(8) Stork, G.; Hill, R. K. *J. Am. Chem. Soc.* **1957**, *79*, 495–500.
(9) Stork, G.; Schulenberg, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 284–292.
(10) Cristol, S. J.; Lalonde, R. T. *J. Am. Chem. Soc.* **1959**, *81*, 1655–1659.
(11) Arnold, D. R.; Trecker, D. J.; Whipple, E. B. *J. Am. Chem. Soc.* **1965**, *87*, 2596–2602.
(12) Franzus, B.; Baird, W. C., Jr.; Chamberlain, N. F.; Hines, T.; Snyder, E. I. *J. Am. Chem. Soc.* **1968**, *90*, 3721–3724.
(13) Franzus, B.; Baird, W. C., Jr.; Surridge, J. H. *J. Org. Chem.* **1968**, *33*, 1288–1290.
(14) Kieboom, A. P. G.; van Rantwijk, F. *Hydrogenation and Hydrogenolysis in Synthetic Organic Chemistry*; Delft University Press: Delft, 1977, and references therein.
(15) Reductions were conducted at –20 °C under 2.4 atm of $D_2$.



**Figure 1.** The ¹H NMR spectrum of norbornane-$d_0$ (bottom) and the ²H NMR spectra of the norbornanes from the reductions by $D_2$ of a mixture of 97% **2** and 3% **1** (middle) and 90% **1** and 10% **2** (top).[16]

mohypostrophene)neopentyl(exo-2-norbornyl)platinum(II) (**1**) and samples containing predominantly (homohypostrophene)neo-pentyl(endo-2-norbornyl)platinum(II) (**2**) according to eq 2.



Np = neopentyl

A: 40% *exo-* + 60% *endo*-2-norbornylmagnesium bromide (the *exo* isomer adds preferentially)

B: *endo*-2-norbornyl-magnesium bromide

Homohypostrophene was chosen to minimize generation of H•ⱼ by loss of hydrogen from the coordinating diolefin; 2-norbornyl is the best understood system with which to study the stereochemistry of carbon–metal bonds; the neopentyl group afforded selectivity toward exo-2-norbornylmagnesium bromide in the addition of a mixture of ca. 40% exo- and 60% endo-2-norbornylmagnesium bromide to (homohypostrophene)neopentyl-platinum(II) chloride (step A of eq 2).

We reduced samples of **1** and **2** with $D_2$ over platinum black in n-pentane[15] and determined the location and number of the deuterium atoms in the resultant norbornanes using ²H NMR and mass spectroscopy.[16] Analysis of the data is lengthy but straightforward and will be detailed separately: the conclusions are summarized in Figure 1. The top spectrum in Figure 1 refers, for example, to the reduction of a mixture of 90% **1** and 10% **2**. The resulting norbornanes contained, on average, 1.1 D in the exo position and 0.1 D in the endo position.

Interpretation of these results in terms of the stereochemistry of the reaction of 2-norbornyl• moieties with D• requires that we know the stereochemistry of formation of the 2-norbornyl• moieties from **1** or **2**. We infer that this initial transformation proceeds with *retention* of configuration at carbon, based on the following data: (i) Stereochemical evidence suggests that the initial adsorption of the organoplatinum complex to the surface occurs *at*

(16) The assignment of the resonances in the ¹H NMR spectrum of norbornane-$d_0$ is well established.[12]

*the platinum center.*[3]    (ii) The reduction of (1,5-cyclo-octadiene)Pt(C₆H₅)₂ ((COD)PtPh₂)—a complex in which transfer with inversion at carbon is not possible—proceeds at a rate comparable to that of the reductions of (COD)PtR₂ (R = Me, Et, *n*-Pr, *i*-Pr, *i*-Bu), complexes in which transfer with inversion at carbon is possible.[2]    (iii) The reduction of (COD)PtNp₂—a complex that generates neopentyl• moieties[17]—also proceeds at a rate comparable to that of the reductions of the (COD)PtR₂ complexes.[2]

We conclude that the reduction of *exo*-2-norbornyl• and *endo*-2-norbornyl• moieties occurs with predominant retention of stereochemistry. The result from the reduction of *exo*-2-norbornyl• appears to be stereochemically straightforward, with the only competing reaction being activation of ca. 20% of the cis C(3)–H (exo) bonds (probably by β-hydride elimination). The reduction of *endo*-2-norbornyl• is more complicated. The observed results are accounted for by a model involving ca. 35% isomerization of *endo*-2-norbornyl• to *exo*-2-norbornyl•, but with the conversion of C• to CD again occurring with retention of stereochemistry.

We have confirmed the structures of **1** and **2** using X-ray crystallography and have characterized (by MS and ¹H NMR) the alkane products of the reductions of **1** and **2**. These details, and their interpretations, will be described separately.

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(17) Displacement with inversion at neopentyl centers is typically much slower than at other alkyl centers. See, for example: Ingold, C. K. *Q. Rev., Chem. Soc.* **1977,** *11,* 1–14.
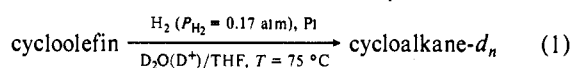
## The Extent of Incorporation of Excess Deuterium in the Platinum-Catalyzed Reduction of Unsubstituted Cycloolefins by H₂ in D₂O/THF Increases with the Strain Energy of the Product Cycloalkanes[1]

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This paper describes the isotopic compositions of cycloalkanes produced by the catalytic reduction of cycloolefins (C*ₙ*H₂*ₙ₋₂*) using H₂ and platinum black in 1:1 v:v THF/D₂O*ₚ*D=1 (eq 1).[2]    We

$$\text{cycloolefin} \xrightarrow[\text{D}_2\text{O(D}^+\text{)/THF, } T = 75\ °\text{C}]{\text{H}_2\ (P_{\text{H}_2} = 0.17\ \text{atm}),\ \text{Pt}} \text{cycloalkane-}d_n \quad (1)$$

conducted the reductions under conditions in which the rate of mass transport of H₂ to the surface of the catalyst limited the rate of reaction.[3,4]    Under these conditions, H• on the surface equilibrates essentially completely with D₂O in solution. Figure 1 summarizes the isotopic compositions of the cycloalkanes.[5]    The

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(2) We chose D₂O/THF (1:1 v:v; pD_{D₂O} = 1) because a survey of solvent systems indicated that this system yielded cyclooctanes having the highest content of deuterium in reductions of cyclooctene.
(3) We performed the reductions in a specially designed round-bottomed flask (volume = 225 mL): a small teat (volume ca. 10 mL) protruded from the bottom of the flask; a Swagelok valve and a rubber septum capped the flask. After charging the teat with a stir bar (3/8 × 3/16 in.) and 40 mg of Pt black, we purged the flask with Ar and added 0.5 mL of dry THF and 0.5 mL of D₂O (adjusted to pD = 1 with D₂SO₄). The apparatus was purged with a mixture of 10% H₂ in Ar for 1 min with stirring; the rate of rotation of the stir bar was 1400 rpm. We pressurized the vessel to 10 psi ($P_{\text{H}_2}$ = 0.17 atm), stirred for 4 min, placed the flask in an oil bath (75 ± 3 °C), and stirred for 5 min. We removed the solvent via cannula and added the substrate (15–20 mg in 3 mL of D₂O/THF) via syringe. Stirring was started and continued for 1 h. Analysis by GC/MS indicated that all reductions were complete.
(4) Miller, T. M.; Izumi, A. N.; Shih, Y.-S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988,** *110*, 3146–3156.
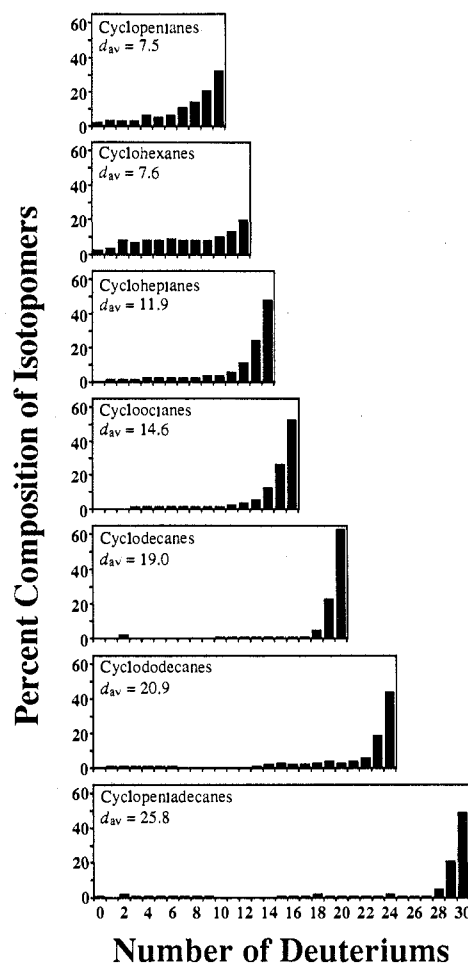


Figure 1. Isotopic distributions and values of $d_{av}$ for the cycloalkanes from the reductions of the corresponding cycloolefins by H₂ and D₂O/THF (1:1 v:v; pD_{D₂O} = 1) over platinum black.[5]  The difference in values of $d_{av}$ from duplicate runs was, in all cases, ≤0.2.
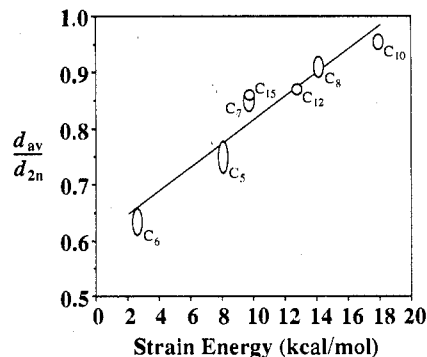


Figure 2. Values of $d_{av}/d_{2n}$ vs strain energies of cycloalkanes (C*ₙ*H₂*ₙ*).[5,17] For consistency, the strain energies are all calculated values, obtained using Macromodel V2.0.[18,19]  The line drawn through the points was determined by linear regression.

important observations are as follows: (1) the isotope of hydrogen found in the cycloalkanes was predominantly that present in D₂O rather than that present in H₂; (2) the cycloalkanes contained deuterium in large excess of that required for stoichiometric

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$$d_{av} = \sum_{n=1}^{m} n(\%\ \text{alkane-}d_n)$$

(6) Miller, T. M.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988,** *110*, 3156–3163.